



Reduction of redox mediators by CO in the presence of a Co porphyrin: Implication for electrochemical cells powered by CO

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HIGHLIGHTS

- We demonstrated that a Co porphyrin can catalyze the reduction of quinones by CO.
- The reaction was confirmed by amperometry, UV-spectroscopy, and gas chromatography.
- The rate of this reaction significantly depended on the redox potentials of quinones.
- This reaction can be regarded as the regeneration of fuel for an indirect CO fuel cell system.

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ABSTRACT

We found that a water-soluble cobalt tetraphenylporphyrin tetrasulfonic acid catalyzes the reduction of redox mediators (quinones and indigo carmine) by CO. The reduction was analyzed by constant-potential amperometry, UV-spectroscopy, and gas chromatography. The rate of this reaction was quantitatively determined by monitoring the reduced forms of these compounds by amperometry. The reduction rate significantly depended on the redox potentials of these compounds. Since the reduced forms of indigo carmine and quinones can act as a good fuel for fuel cells, this reaction can be regarded as the conversion of the fuel from CO to other redox active species.

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1. Introduction

The hydrogen that is used in a proton exchange membrane fuel cell (PEMFC) is produced by the steam reformation of hydrocarbons. CO is also generated from this process. The ratio of CO/H₂ in the anode gas is especially high when biomass is used as a fuel [1]. CO could be used as a power source for PEMFCs. However, it can be difficult to use CO as a power source for PEMFCs, since CO poisons Pt-based anode catalysts of PEMFCs [2].

Despite the difficulty, the use of CO as a fuel for PEMFCs has been investigated. It has been demonstrated that Rh porphyrins can catalyze CO at low overpotentials [3–7]. We previously reported a direct CO-PEMFC that used an Rh porphyrin as an anode catalyst [4]. On the other hand, an indirect CO fuel cell has also been described [1]. In this system, a redox active species such as

polyoxometalate acts as a fuel, and the used species are regenerated by CO in the presence of an Au catalyst. Polyoxometalate works as a redox mediator in this system, and the overall system can be regarded as an indirect CO fuel cell system.

Both of direct and indirect CO fuel cells have advantages and disadvantages. Direct CO fuel cells have a simple structure, and exhibit high power. However, the catalyst is virtually limited to Rh complexes [3–8]. The amount of catalyst cannot be drastically increased in the direct system since catalysts must be situated only on the boundary. While indirect CO fuel cell systems have complex structures, a large space is available for electron transfer from CO to redox active species. Due to this large space, the amount of catalyst in an indirect system can be increased.

Recently, it was reported that an Rh porphyrin can catalyze electron transfer from CO to indigo carmine [9]. This compound can catalyze complete conversion of CO to CO₂. While this catalyst was applied to selective CO removal for fuel cells, it might also be used in an indirect CO fuel cell system because of its high activity. However, this catalyst uses precious rhodium. Since the amount of

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a catalyst in an indirect CO fuel cell system can be increased, the use of a noble metal catalyst is not necessary. If we made much account of the benefit of indirect CO fuel cell systems, a non-noble metal complex might be a more favorable candidate. Besides an Rh complex, a certain kind of Pd complex is also reported to catalyze the reduction of quinones by CO [10]. However, there is little information available on the use of non-noble metal catalysts for this reaction.

From these backgrounds, we selected a Co porphyrin in place of an Rh porphyrin. A Co porphyrin exhibited activity for CO electro-oxidation in aqueous solution [11], although the overpotentials were larger than those with Rh porphyrin. We used water-soluble Co(III) tetraphenylporphine tetrasulfonic acid (Co-TPPS) as a catalyst for electron transfer from CO to the redox mediators.

As a redox mediator, we examined quinones and indigo carmine. These compounds exhibit reversible cyclic voltammograms, which indicates that their reduced forms are easily reoxidized by an electrode. It has been demonstrated that quinones and indigo carmine function as active materials in batteries [12,13]. In fuel cell systems, ascorbic acid, which has a diketone structure similar to quinone, acts as a fuel [14]. These previous studies suggest that quinones and indigo carmine also act as redox mediators in an indirect CO fuel cell system. The overall system is shown in Scheme 1. The chemical structures of compounds used in this study are shown in Scheme 2.

If we use a Co porphyrin in place of an Rh porphyrin, the catalytic activity would decrease significantly compared to the system of Rh porphyrin [9] because the electrocatalytic activity of the former is much lower than that of the latter. Hence, we have to quantitatively analyze slow reactions. We adopt an electrochemical method (constant-potential amperometry). This method can monitor the concentration of reduced forms of quinones, and hence determine the reaction rate quantitatively and easily even if it is slow [15,16].

Rh porphyrin can catalyze the reduction of indigo carmine that has the low redox potential with a high rate [9]. This is desirable for indirect CO fuel cell. However, Co porphyrin might not use such negative mediators due to its low activity, and more positive mediators might be needed. Then, for the application to the indirect CO fuel cell, we also analyze the relationship between the rates and the redox potentials of these redox mediators. Based on the relationship, we can find the best quinone for an indirect CO fuel cell.

In this report, we demonstrate that Co-TPPS can catalyze the reduction of quinone by CO. The reaction was analyzed by amperometry, UV-spectroscopy, and gas chromatography. Some kinetic

analyses were carried out and a plausible reaction mechanism was presented. We also examined the reduction rate of several quinones and indigo carmine, and selected favorable mediators for an indirect CO fuel cell based on the relationship between the rates and redox potentials.

2. Experimental section

2.1. Materials

Co(III) tetraphenylporphine tetrasulfonic chloride (Co-TPPS) was purchased from Frontier Scientific and used as received. 2-Methyl-1,4-naphthoquinone (vitamin K₃, VK₃), 1,4-naphthoquinone (NQ), sodium 1,2-naphthoquinone-4-sulfonate (NQS), 5-hydroxy-1,4-naphthoquinone (HNQ), disodium 1,4-anthraquinone-2,6-disulfonate (AQS), and 5,5'-Indigodisulfonic acid sodium salt (indigo carmine, IC) were purchased from Tokyo Kasei Kogyo. The concentration of Co-TPPS was determined by UV–vis spectroscopy based on its molar extinction coefficient ($2.85 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 435 nm in DMSO) [17].

2.2. Electrochemical measurements

Electrochemical measurements were performed with an ALS electrochemical analyzer (Model 627B). A three-electrode electrochemical system was used for all of the measurements. The volume of a reaction vessel was fixed at 13 mL. A glassy carbon electrode was used as a working electrode. An Ag|AgCl|KCl (sat.) and a platinum electrode were used as a reference and counter electrodes, respectively. The potential was converted to the potential vs. a reversible hydrogen electrode (RHE) as described in literature [5].

All electrochemical measurements were performed in 0.1 M H₂SO₄ at 55 °C. To determine the redox potentials of redox mediators at 55 °C, cyclic voltammograms were measured in 0.1 M H₂SO₄ under an argon atmosphere at a scan rate of 10 mV s⁻¹.

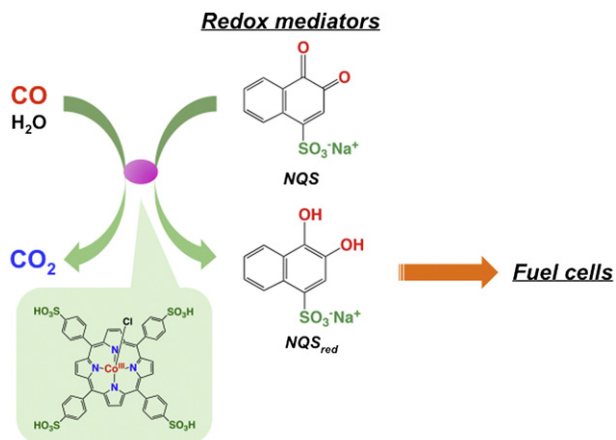
2.3. Constant-potential amperometry

The potentials used to monitor the reduced forms of NQS, NQ, VK₃, HNQ, IC and AQS were 0.6 V, 0.5 V, 0.3 V, 0.3 V, 0.15 V, and 0.15 V vs. Ag|AgCl|KCl (sat.), respectively. The working electrode was rotated at 3600 rpm. For the measurements of the proportion coefficient between anodic current and the concentration of the reduced forms of redox mediators, a 0.1 M H₂SO₄ solution containing quinone was purged with H₂ gas, and H₂ gas was continuously flowed during the measurements (the results are shown in Section 3.1). For the measurements of the reduction of the redox mediators by CO, a 0.1 M H₂SO₄ solution containing Co-TPPS was purged with CO before the measurements. During the measurements, CO gas was flowed continuously.

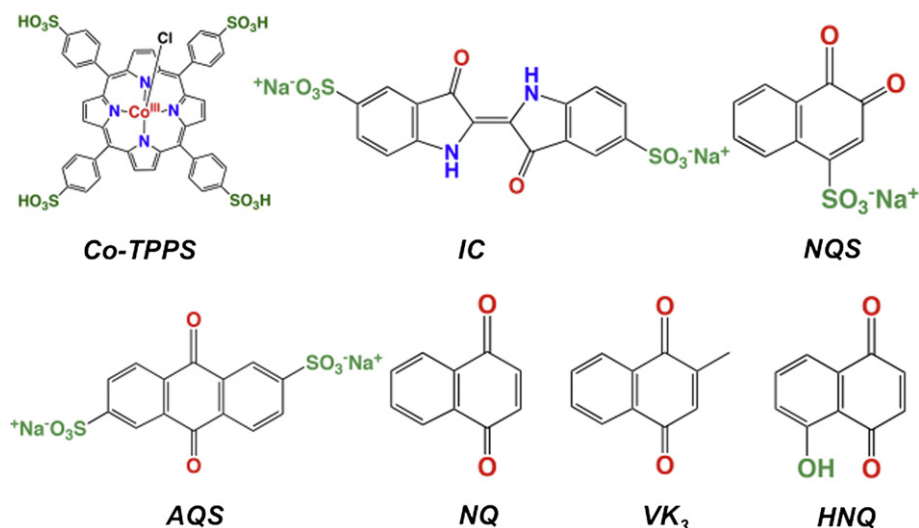
Quinones and indigo carmine were dissolved in a solvent at a high concentration (10 mM). As a solvent, acetone was used for VK₃ and NQ, and water was used for other compounds. A portion of this stock solution was added into a test solution at 0.5%. The concentrations of quinones were set at 0.05 mM unless mentioned otherwise. The concentration of Co-TPPS was 0.01 mM for VK₃, NQ, HNQ, and NQS, and 0.1 mM for the measurement of AQS and IC.

2.4. UV spectroscopy

UV spectroscopy was performed with Shimadzu UV-1500 PC photodiode array spectrophotometer equipped with a quartz cell (light path = 1 cm). The reduction of NQS with CO was carried out as follows; NQS (0.1 mM) was added into 0.1 M H₂SO₄. The cell was sealed with a silicon plug, and purged with CO. Then, Co-TPPS



Scheme 1. Schematic representation of an indirect CO fuel cell system.



Scheme 2. Chemical structures of Co-TPPS and redox mediators used in this study. Co-TPPS: Co(III) tetraphenylporphine tetrasulfonic chloride, IC: 5,5'-indigodisulfonic acid sodium salt (indigo carmine), NQS: sodium 1,2-naphthoquinone-4-sulfonate, AQS: disodium 1,4-anthraquinone-2,6-disulfonate, NQ: 1,4-naphthoquinone (vitamin K₃), and HNQ: 5-hydroxy-1,4-naphthoquinone.

(1.1 μM) was added into the solution, and change of spectra was recorded after the addition of Co-TPPS. The measurements were carried out at 55 $^{\circ}\text{C}$.

The reduction of NQS with H₂ was performed as follows; NQS (0.1 mM) was added into 0.1 M H₂SO₄. The Pt wire was immersed in the solution, and H₂ gas was passed through for 10 min. The cell was incubated for 10 min at 55 $^{\circ}\text{C}$, and a spectrum was recorded.

2.5. Product analysis by gas chromatography

The solution (15 mL) (10 mM NQS and 0.05 mM Co-TPPS in 0.09 M H₂SO₄) was placed in a reaction vessel (the volume of gas phase = 19.5 mL). The vessel was sealed with a rubber plug, and then purged with CO. After the vessel was incubated at 25 $^{\circ}\text{C}$ for 60 min, the gas phase was analyzed by a gas chromatograph (Shimadzu GC 2014) with a TCD detector.

3. Results and discussion

3.1. Monitoring of the reduced form of quinones and indigo carmine

First, we set up the method by which the concentration of the reduced forms of redox mediators is monitored. The concentrations

were monitored by constant-potential amperometry as described in the literature [15,16] with some modifications. The potentials used to monitor the reduced forms of the mediators were at least 0.1 V higher than the redox potentials of them. The working electrode was rotated at a sufficiently high rotation rate. Under these conditions, anodic current is determined by diffusion, and is proportional to the concentration of the reduced form of redox mediators. Details are described in [Experimental section](#).

To determine the reaction rate quantitatively, the proportion coefficients between anodic currents and concentrations have to be determined. It is difficult to isolate the reduced forms, since some of them are easily reoxidized by air. Hence, we determined the coefficient by the *in situ* reduction method as follows.

A platinized Pt was immersed in 0.1 M H₂SO₄, and was not attached to a working, reference, or counter electrode. Amperometry at the potential mentioned above was performed. Under a hydrogen atmosphere, a quinone or IC was added. A current–time curve for NQS is shown in [Fig. 1A](#) as an example. The added compounds were gradually reduced by H₂, and the anodic current increased. All of the compounds were then reduced, and the current reached a steady state.

The increase in anodic current was plotted as a function of the concentration of added mediators. The plot for NQS is shown in

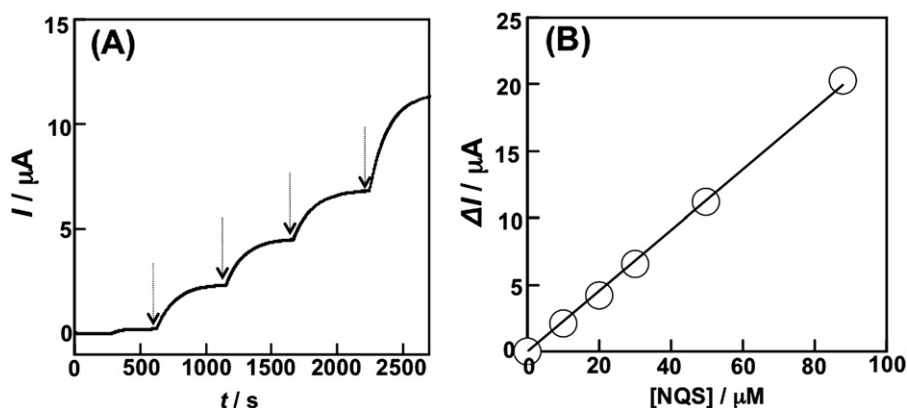


Fig. 1. (A). Monitoring of the reduced form of NQS (NQS_{red}). The arrows show the successive addition of NQS: 10 μM , 10 μM , 10 μM , and 20 μM . The measurement was performed in 0.1 M H₂SO₄ containing platinized Pt under a H₂ atmosphere at 55 $^{\circ}\text{C}$. The electrode was rotated at 3600 rpm. (B). A standard curve for the anodic current and the total concentration of NQS.

Fig. 1B, which depicts a relationship between the current and the concentration of the reduced form of NQS (NQS_{red}). The proportion coefficient was determined. Thus, the concentrations of reduced forms of the redox mediators were successfully monitored. The current in the amperometry was converted to the concentration of the reduced forms using this coefficient.

3.2. Reduction of NQS by CO with Co-TPPS

The concentration–time curve in Fig. 2A shows the reduction of NQS by CO in the presence of Co-TPPS. The test solution was CO-saturated 0.1 M H_2SO_4 that contains Co-TPPS (0.01 mM). Upon the addition of NQS into this solution, the anodic current (i.e. the concentration of the reduced form of NQS (NQS_{red})) rapidly increased (Fig. 2A) [18]. The slope of the line corresponds to the rate of the reaction. The initial rate was calculated to be $0.66 \mu\text{M s}^{-1}$ under these conditions. The added NQS (50 μM) was almost completely reduced to its reduced form. The reason of slight difference between the concentrations of added NQS and generated NQS_{red} remains unclear. It might be attributed to possible complex formation of NQS_{red} and Co-TPPS.

The concentration–time profile for NQS_{red} is linear with time (Fig. 2A). This means that the rate of the reduction of NQS is almost constant independent of the concentration of NQS. In fact, the rate of the reduction of 0.5 mM NQS ($0.68 \mu\text{M s}^{-1}$, Fig. 2B) were almost equal to that of 0.05 mM NQS ($0.66 \mu\text{M s}^{-1}$, Fig. 2A). The independency of the rate on [NQS] suggests that Co-TPPS forms a complex with NQS, and that the binding constant is high.

We also examined the dependence of the rate on the concentration of Co-TPPS. Fig. 3 shows a plot of the rate of the reduction of NQS vs. [Co-TPPS]. The rate increased linearly with the increase of [Co-TPPS]. The plot clearly shows that this reaction obeys first-order kinetics with regard to [Co-TPPS]. This suggests that Co-TPPS works as a catalyst.

3.3. UV–vis spectroscopy and gas chromatography

The reduction was also confirmed by UV–vis spectroscopy (Fig. 4). Under a CO atmosphere, the spectrum of NQS changed on the addition of Co-TPPS. The absorbance at around 370 nm decreased, and that around at 300 nm increased with an isosbestic

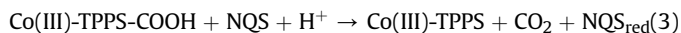
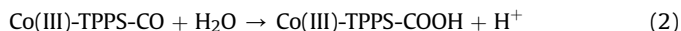
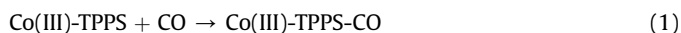
point at 347 nm. NQS_{red} , which was generated by H_2 -reduction in the presence of Pt catalyst, exhibits almost the same spectrum as line (e), indicating that NQS_{red} was generated by CO-induced reduction of NQS in the presence of Co-TPPS.

Generated CO_2 from the reaction of NQS and CO in the presence of Co-TPPS was detected by gas chromatography. After the reaction, CO_2 (4.7 μmol) was detected in the gas phase. Based on the solubility of CO_2 and the volume of the solution, the amount of CO_2 in the solution was 3.0 μmol . Hence, the total amount of CO_2 generated reached 7.7 μmol (The initial amount of CO and NQS was fixed at 812 μmol and 150 μmol) CO_2 was not detected from the NQS solution without Co-TPPS. All of these results support the notion that Co-TPPS catalyzes the reduction of NQS by CO.

3.4. A possible reaction mechanism

Shi et al. [11] revealed that the trivalent form of cobalt (Co(III)) play a central role in the electrocatalytic CO oxidation by Co porphyrin. CO is coordinated on Co(III) in a Co porphyrin. In the electrochemical reaction, Co(III) is generated electrochemically from Co(II). In contrast, Co(III) would exist *ab initio* in our system since we use Co-TPPS that contains the trivalent form of cobalt (Co(III) tetraphenylporphine tetrasulfonic chloride).

We postulate a reaction mechanism as follows.



First, CO coordinates on Co(III)-TPPS and Co(III)-COOH complex is formed (Eqs. (1) and (2)). This process coincides with the mechanism reported in Ref. [11]. Second, Co(III)-COOH would give electrons to NQS to generate free Co(III)-TPPS, CO_2 , and NQS_{red} . It was reported that the electron transfer from Co(II)TPP to *p*-benzoquinone is greatly activated by the presence of metal cation [19] or hydrogen bond formation in nonaqueous solvent [20]. Such activation implies the participation of Co(II) species in the reaction. However, in this aqueous system, it is unclear whether such enhancement effects on electron transfer are significant, and hence

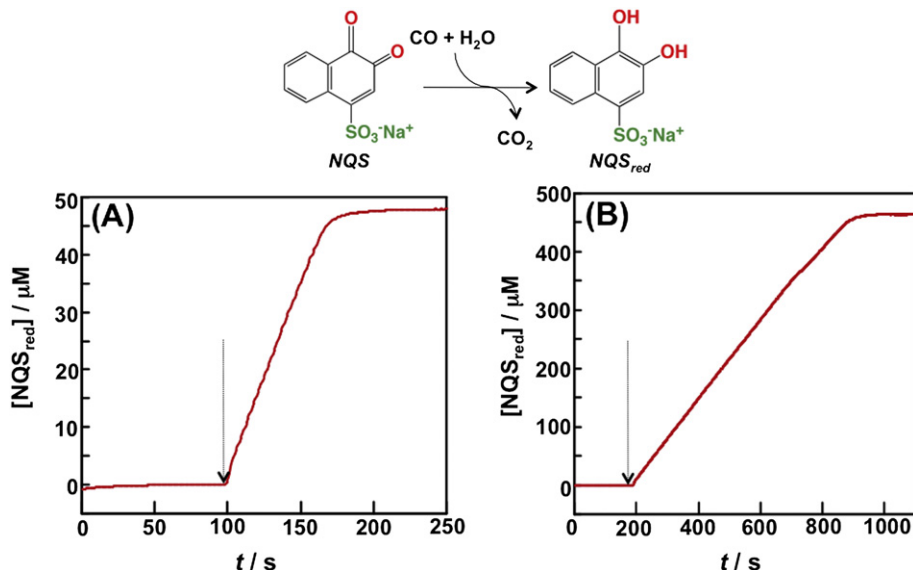


Fig. 2. Concentration–time profile of the reduction of NQS by CO in the presence of Co-TPPS. The arrow shows the addition of NQS ((A) 0.05 mM and (B) 0.5 mM). The concentration of Co-TPPS was set at 0.01 mM. The measurement was performed in 0.1 M H_2SO_4 under a CO atmosphere at 55 °C.

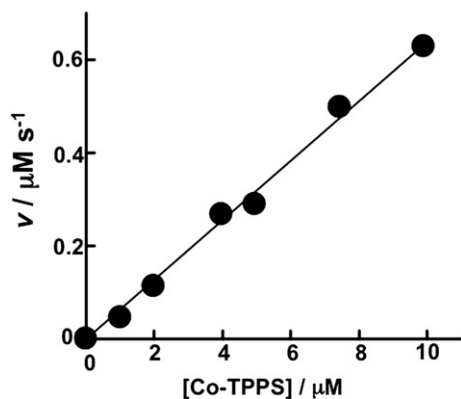


Fig. 3. A plot of the rate of NQS reduction by CO vs. the concentration of Co-TPPS.

the participation of Co(II) species in the reaction remains obscure. Further investigation is needed to identify the intermediate. Before the electron transfer, Co-TPPS and NQS might form a complex, as suggested by the concentration-dependence of NQS. Weak intermolecular complexes of cobalt porphyrin and naphthoquinone were reported [21]. The formation of the complex is favorable for the electron transfer.

3.5. Relationship between the reduction rate and the redox potentials of redox mediators

To obtain the relationship between the rates and redox potentials of quinone, we evaluated reduction rates of other quinones by the same method of Fig. 2. The logarithms of the rates per 0.01 mM Co-TPPS were plotted as a function of the redox potentials of quinones and IC (Fig. 5) [22]. The redox potentials were determined by cyclic voltammetry.

The rate depended on the redox potential as expected. The rate increased with an increase in the redox potential up to ca. 0.35 V, and approached an almost constant value above ca. 0.35 V (Fig. 5). In the “increase region”, electron transfer to the redox mediators would play a role in the rate-determining step. In the “constant region”, the rate is controlled by other process such as water

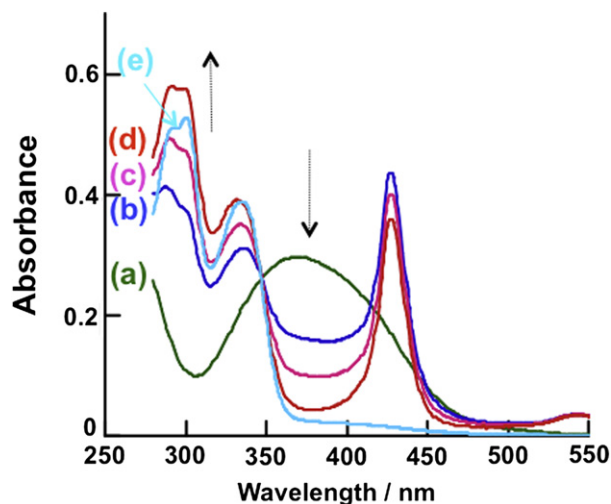


Fig. 4. Change in UV spectra with NQS reduction. The measurement was performed in 0.1 M H₂SO₄ under a CO atmosphere at 55 °C. Line (a) indicates a spectrum of NQS. Lines (b)–(d) indicate spectra (b) 1700 s, (c) 2000 s, and (d) 2400 s after the addition of Co-TPPS. Line (e) indicates a spectrum of NQS_{red}, which is generated by H₂-reduction in the presence of a Pt wire.

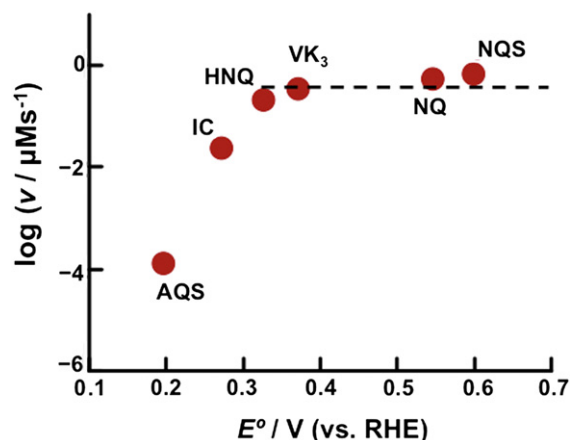


Fig. 5. Logarithms of rates of the CO oxidation were plotted as a function of redox potential (E°) of quinones and indigo carmine. The rates were measured with the same method as Fig. 2. The concentration of quinones was fixed at 50 μM.

addition to CO molecule (Eq. (2)) and/or CO addition on Co-TPPS (Eq. (1)).

The potential dependence provided insight regarding the mediator that should be used in an indirect CO fuel cell system. If this reaction is used in an indirect CO fuel cell system, a lower redox potential is better. However, the reaction drastically decreased with the decrease in the redox potential below 0.35 V. This trade-off relationship suggests that IC or HNQ is the best compound for the indirect CO fuel cell system among the compounds tested.

4. Conclusion

We have found that a water-soluble Co porphyrin acts as a catalyst for the reduction of quinones by CO. This reaction can be regarded as the regeneration of fuel in an indirect CO fuel cell system, since the reduced forms of these compounds can act as a fuel for fuel cells. The reaction was monitored by amperometry. The dependence of the rate on the concentrations of a quinone and a Co porphyrin was also analyzed. This reaction was also confirmed by gas chromatography and UV-spectroscopy. Based on the results, a plausible reaction mechanism was presented. The rate significantly depended on the redox potentials of quinones.

In this system, CO, which is difficult to use as a fuel, was converted to redox mediators that can easily communicate with electrodes even without electrocatalysts. The catalyst in this conversion does not contain a noble metal. Compared to the previous catalysts using Rh [9] or Pd [10], the limitation of resource is counteracted in our system. Due to this advantage, the amount of the catalyst can be increased, and the rates of the conversion can also be increased. This conversion with a non-noble metal catalyst expands the possibility of electrochemical devices powered by CO.

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References

- [1] W. Kim, T. Voigt, G. Rodriguez-Rivera, J. Dumesic, *Science* 305 (2004) 1280–1283.
- [2] R. Lemons, *J. Power Sources* 29 (1990) 251–264.
- [3] J.F. van Baar, J.A.R. van Veen, N. de Wit, *Electrochim. Acta* 27 (1982) 57–59.
- [4] S. Yamazaki, T. Ioroi, Y. Yamada, K. Yasuda, T. Kobayashi, *Angew. Chem. Int. Ed.* 45 (2006) 3120–3122.

- [5] S. Yamazaki, Y. Yamada, S. Takeda, M. Goto, T. Ioroi, Z. Siroma, K. Yasuda, *Phys. Chem. Chem. Phys.* 12 (2010) 8968–8976.
- [6] S. Yamazaki, M. Yao, Z. Siroma, T. Ioroi, K. Yasuda, *J. Phys. Chem. C* 114 (2010) 21856–21860.
- [7] S. Yamazaki, M. Yao, S. Takeda, Z. Siroma, T. Ioroi, K. Yasuda, *Electrochem. Solid-State Lett.* 14 (2011) B23–B25.
- [8] J. Wu, C.P. Kubiak, *J. Am. Chem. Soc.* 105 (1983) 7456–7457.
- [9] J. Biffinger, S. Uppaluri, H. Sun, S. DiMaggio, *ACS Catal.* 1 (2011) 764–771.
- [10] C. Querci, R. D'Aloisio, R. Bortolo, M. Ricci, D. Bianchi, *J. Mol. Catal. A Chem.* 176 (2001) 95–100.
- [11] C. Shi, F. Anson, *Inorg. Chem.* 40 (2001) 5829–5833.
- [12] M. Yao, M. Araki, H. Senoh, S. Yamazaki, T. Sakai, K. Yasuda, *Chem. Lett.* 39 (2010) 950–952.
- [13] M. Yao, H. Senoh, S. Yamazaki, Z. Siroma, T. Sakai, K. Yasuda, *J. Power Sources* 195 (2010) 8336–8340.
- [14] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, T. Kobayashi, *Electrochem. Solid-State Lett.* 6 (2003) A257–A259.
- [15] T. Ikeda, T. Kurosaki, K. Takayama, K. Kano, K. Miki, *Anal. Chem.* 68 (1996) 192–198.
- [16] S. Yamazaki, T. Kaneko, N. Taketomo, K. Kano, T. Ikeda, *Appl. Microbiol. Biotechnol.* 59 (2002) 72–78.
- [17] K. Yamamoto, S. Nakazawa, A. Matsufuji, T. Taguchi, *J. Chem. Soc. Dalton Trans.* (2001) 251–258.
- [18] Co-TPPS did not cause significant continuous increase in the anodic current without NQS under a CO atmosphere (data not shown).
- [19] S. Fukuzumi, K. Ohkubo, *Chem. Eur. J.* 6 (2000) 4532–4535.
- [20] S. Fukuzumi, H. Kitaguchi, T. Suenobu, S. Ogo, *Chem. Commun.* (2002) 1984–1985.
- [21] L. Ford, H.A.O. Hill, B.E. Mann, P.J. Sadler, R.J.P. Williams, *Biochim. Biophys. Acta* 430 (1976) 413–418.
- [22] The rate drastically differed with the quinones used, and hence [Co-TPPS] was changed to determine the rate accurately according to the quinones. The rates were normalized by [Co-TPPS]. A linear relationship between the rates and the concentration of Co-TPPS (Fig. 3) allows us to carry out such normalization.